doi:10.1017/S1431927617002999
Microsc. Microanal. 23 (Suppl 1), 2017

Etching and Mending of Graphene Edges by Cu and Pt Atoms

Emi Kano[1, 2, *], Ayako Hashimoto[1, 2, 3, 4] and Masaki Takeguchi[1, 2, 4]

[1.] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.
[2.] In-situ Characterization Technique Development Group, National Institute for Materials Science, Tsukuba, Japan.
[3.] Global Research Center for Environment and Energy based on Nanomaterials Science, National Institute for Materials Science, Tsukuba, Japan.
[4.] Transmission Electron Microscopy Station, National Institute for Materials Science, Tsukuba, Japan.

Introducing foreign elements into graphene strongly affects its electronic and chemical properties, especially when the atoms are strongly bonded to the graphene edges or vacancies. However, it can also result in etching. While this phenomena generally decrease mechanical strength and electrical conductivity of graphene, it offers a promising method for producing graphene nanoribbons, as metal nanoparticles can etch graphene along a specific crystallographic direction [1]. Only a few experimental reports have been published so far discussing activity of metal atoms on graphene. It is therefore essential to visualize the interaction of graphene with different chemical elements to clarify the effects of metal atoms on graphene structure.

Aberration-corrected transmission electron microscopy (TEM) enables us to image the structures and interaction dynamics between metal atoms and graphene edges at the atomic scale in real time. Most metal atoms were experimentally reported to etch graphene under electron beam irradiation [2]. To the best of our knowledge, there are no reports on the direct observation of single-atom metal catalysis of mending or reconstruction of graphene structure. Although Au [3] and Fe [4] atoms were observed at graphene edges and electron irradiation resulted in the removal or addition of a few C atoms around the impurity atoms, the edge structure did not change significantly.

Here we present different behaviors of Cu, Pt and Au atoms at graphene edges. We have found opposite effects of Cu ant Pt atoms on graphene edges: Cu atoms mend graphene edges, but Pt atoms etch them. Au atoms promote neither etching nor mending and move away from graphene edges.

Single-layer graphene was transferred onto *in situ* heating chips (E-chips for Aduro™, Protochips). Metals were then deposited on graphene using an ion beam etching system (PECS, Gatan) for Cu, DC plasma sputtering system (JFC-1600, JEOL) for Pt and electron beam deposition system (RDEB-1206K, R-DEC) for Au. We minimized hydrocarbon contamination by *in situ* heating inside a TEM column at ~10^{-5} Pa. The microscope (JEM-ARM 200F, JEOL) was operated at 80 kV to reduce knock-on damage to graphene samples.

The 80 keV energy electrons can transfer up to ~15.7 eV to C atoms. While this value is lower than the knock-on threshold in perfect graphene, it is sufficiently high to dislocate or remove atoms at graphene edges. First, we applied a relatively high electron beam current density j to create small pores in graphene. Then we observed metal atoms at the pore edges at 150 or 300 °C and j = 63–1000 A/cm^2. The electron density strongly affected the dynamics of C atoms at graphene edges.

Figure 1 shows Cu-mediated mending of the graphene edge under electron irradiation for ~100 s. We previously reported that substitutional Cu atoms can promote rotations of C–C bonds in the graphene lattice [5]. C–C bond rotations can convert pairs of five- and seven-membered rings into six-membered rings. Such rotations also occurred with the movement of Cu atoms at the edge. Stable Cu atoms then trapped additional C atoms, which were presumably etched by electron beam from the nearby edges or amorphous carbon contamination and diffused along the edge. The C–C bond rotations occurred before and after the trapping of additional C atoms and thereby mended the graphene edges.

Figure 2 shows Pt-mediated etching of the graphene edge under electron irradiation for ~75 s. Pt atoms moved into a vacancy at the edge, which was too small for accommodating a Pt atom, and hence the nearby C atoms were strained and pushed aside. This strain or defect reduces the knock-on threshold and thereby promotes etching. Sputtered C atoms diffused along the edge, but continuous electron irradiation moved them outside the view soon. After that, the Pt atom moved into the created vacancies, repeating the etching process in a new location.

These transformations were promoted by electron irradiation, while the effect of heating between 150 and 300 °C was less pronounced. Cu and Pt atoms formed different configurations in graphene and induced opposite effects. Our results suggest that deposition of different metals on graphene edges, combined with electron irradiation, allows us to control the edge structure.

References:
[1] S. S. Datta et al. Nano Lett. **8** (2008), 1912–1915.
[2] Q. M. Ramasse et al. ACS Nano **6** (2012), 4063–4071.
[3] H. Wang et al. Nanoscale **4** (2012), 2920–2925.
[4] J. Zhao et al. Proc. Natl. Acad. Sci. **111** (2014), 15641–15646.
[5] E. Kano et al. Nanoscale **8** (2016), 529–535.
[6] A part of this work was supported by "Nanotechnology Platform Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and JSPS KAKENHI Grant Numbers 15J04118, 25390035 and 16H03875, Japan.
[7] First author will move after the graduation: National Institute of Nanotechnology, 11421 Saskatchewan Drive, Edmonton, Canada.

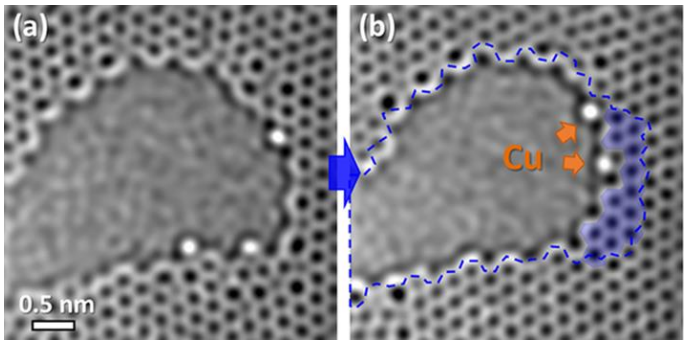

Figure 1. Low-pass filtered TEM images (**a**) before and (**b**) after the Cu-mediated mending of graphene edge. Atoms appear bright since the images were taken under overfocus condition.

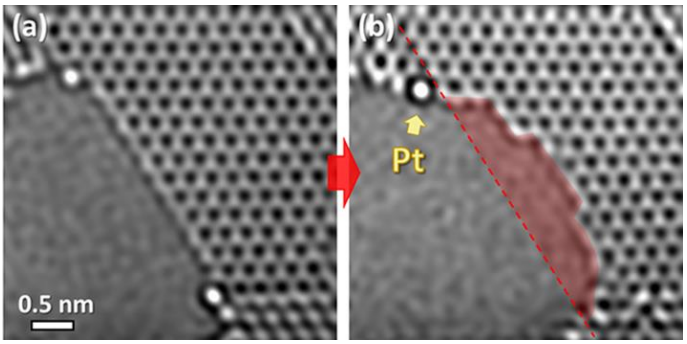

Figure 2. Low-pass filtered TEM images (**a**) before and (**b**) after the Pt-mediated etching of graphene edge. Pt atoms appear brighter than Cu atoms.

https://doi.org/10.1017/S1431927617002999 Published online by Cambridge University Press